



Investigation of potassium doped mixed spinels $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ as catalysts for an efficient N_2O decomposition in real reaction conditions

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ABSTRACT

The influence of copper in the mixed spinel $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ on the catalytic activity in N_2O decomposition was investigated under ideal and real reaction conditions. A strong dependency of the catalytic activity on the amount of Cu in $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ catalysts was observed. Decreasing the amount of Cu increases the catalytic activity. Aiming for improved activity the influence of doping with alkaline (earth) metals was investigated. The use of potassium as dopant allowed a further increase of the catalysts activity. High activity was found for $\text{K}-\text{Cu}_{0.25}\text{Co}_{2.75}\text{O}_4$ and full conversion was already reached at 330 °C under ideal conditions. The effect of O_2 , NO and H_2O in the gas mixtures on the decomposition of N_2O was evaluated. Overall, full N_2O decomposition could be reached at temperatures as low as 490 °C in realistic reaction conditions. Additionally, stability tests emphasise stable activity for at least 60 h. Furthermore, no irreversible deactivation even in the presence of NO, O_2 and H_2O was found. The catalysts were fully characterised by means of XRD, elemental analysis, TGA, TPR and N_2 -physisorption. TPD- O_2 measurements were performed to investigate the influence of the catalyst composition on oxygen vacancies to elucidate the nature of active sites.

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1. Introduction

Nitrous oxide (N_2O) contributes to the depletion of the ozone layer [1], and contributes to the greenhouse effect due to its high ability to absorb and backscatter thermal radiation to the earth. Thus, it poses a huge global warming potential. N_2O has a 310 times larger global warming potential than CO_2 [2]. Major amounts of N_2O in the environment are of natural origin, while 35% of all emissions origin from anthropogenic sources. Especially chemical processes, such as the production of adipic acid and nitric acid or processes applying nitric acid as oxidising agent contribute to anthropogenic N_2O emissions. Considering a lifetime of nitrous oxide in the atmosphere of 150 years, a reduction of their emission from industrial sources is indispensable [3]. A promising way to decrease N_2O emissions from e.g. HNO_3 production is the catalytic decomposition of nitrous oxide into nitrogen and oxygen in a tertiary alignment [3]. Therefore, many types of catalysts such as supported noble metals [4–9], metal oxides [10–16] and ion-exchanged zeolites [17–19] were tested. Most of them suffer from deactivation in the

presence of O_2 , NO and H_2O in the reactant stream or they require high temperatures for high conversions. So far only Fe-ZSM-5 shows sufficient activity and stability for industrial application [20]. Nevertheless, current operation temperatures of around 450 °C are still quite high compared to the temperatures of the exhaust gases.

Beside iron containing zeolites, cobalt based spinels ($\text{A}^{\text{II}}\text{B}^{\text{III}}_2\text{O}_4$) bear a high potential as feasible catalysts for N_2O decomposition. In these materials, oxygen atoms form a fcc lattice in the unit cell. In a regular spinel, the atom on the A site is typically a divalent metal ion which is tetrahedrally coordinated by oxygen atoms. The B atom is usually octahedrally coordinated with an oxidation state of +III. Also inversion and partial inversion of the occupation of sites is possible. The presence of a mixture of oxidation states the use of varying metal atoms, and changes in the metal environment make this material class highly suitable for a selected adjustment of the properties for an enhanced N_2O decomposition. Russo et al. investigated the activity of Co_3O_4 in N_2O decomposition and compared the activities with metal exchanged MCo_2O_4 ($\text{M}=\text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) [21]. They discovered that introducing Mg and Zn highly increases the activity and reduces the deactivation by oxygen. Therein, temperatures to reach 50% N_2O conversion ($T_{50\%}$) under ideal conditions were 440 and 475 °C for MgCo_2O_4 and ZnCo_2O_4 , respectively [21]. Yan et al. confirmed that

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the degree of metal exchange in $M_xCo_{3-x}O_4$ ($M = Mg, Ni, Zn$) has a huge influence on the catalytic performance of the spinel materials [22,23]. Stelmachowski et al. claimed that the introduction of Zn into Co_3O_4 lowers the barrier for electron excitation from the Fermi level [24]. The effectiveness of double promotion was already shown with a K doped and Zn modified cobalt spinel which was prepared in a larger scale for testing in a pilot plant. The laboratory scale catalyst showed the same performance as the large scale catalyst with a $T_{50\%}$ -value of 275 °C in ideal reaction conditions. On the pilot plant, the catalyst showed high and stable conversion rates in the presence of O_2 , NO and H_2O at 350 °C [25,26].

From batch decomposition experiments Srinivasan and Sundararajan showed that the catalytic activity of $Cu_xCo_{3-x}O_4$ is dependent on the degree of exchange of Co by Cu [27]. This was later emphasised by Abu-Zied et al. for continuous operation conditions [28]. In their study, Abu-Zied et al. prepared catalysts by coprecipitation with K_2CO_3 whereby high amounts of K remained in the final catalysts [28]. Ohnishi et al. and Asano et al. described that doping with trace amount of alkaline metals, especially K, highly increases catalytic activity [29,30]. Consequently, the study of Abu-Zied et al. reflects the influence of Cu in combination with K [28]. Conclusions on the exclusive contribution of the Cu content on the catalytic activity are hardly possible. Overall, they observe maximum activity for high Cu amounts in the catalyst associated with an increasing K content. In the study of Asano et al., an optimal K/M ratio of 0.02 was identified for Co_3O_4 as catalyst [30]. Another study of Dou et al. focusses on the influence of the potassium precursor for $Cu_{0.8}Co_{2.2}O_4$ indicating an optimal molar ratio for K doping of 0.05 with K_2CO_3 as precursor [31]. The positive influence of the addition of K to Co_3O_4 was already described by Haneda et al. for the NO decomposition [32]. They explained the behaviour as follows: due to doping, a donation of electrons from the alkali metal to transition metals takes place and weakens the Co–O bond. Thus, it facilitates the reduction of Co^{3+} towards Co^{2+} . Therefore, more active Co^{2+} atoms appear on the surface of the catalyst [32]. Zasada et al. correlated the decrease in catalysts work functions due to potassium doping with the catalytic activity in N_2O decomposition. They described that a lower work function of the catalysts results in facilitated redox processes between the active species and adsorbed N_2O intermediates. Furthermore, they elucidated that the most preferred sites for K atoms on the surface are interstitials between two tetrahedral Co atoms [33].

Considering the nature of active sites in N_2O decomposition, either oxygen vacancies or metal centres are discussed as potential active sites for the catalytic decomposition of N_2O [4].

In general, it is proposed that N_2O adsorbs dissociative on the active centre (1) whereby N_2 is desorbed while an adsorbed oxygen species (adsorbed species marked with *) stays at the surface of the catalyst Desorption of adsorbed O species can either occur via a Langmuir–Hinshelwood (2) or a Eley–Rideal mechanism (3) (Scheme 1). In the Langmuir–Hinshelwood mechanism, the adsorbed oxygen species migrate on the surface until two oxygen atoms meet, combine to molecular oxygen, and desorb. This occurs under restoring of the active centre. In the Eley–Rideal mechanism, a N_2O molecule from the gas phase reacts with an adsorbed oxygen atom whereby N_2 and O_2 desorb by restoring of the active species.

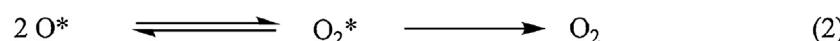
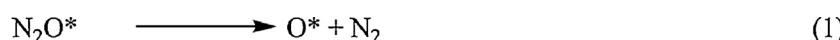
The literature about the kind of metal centre which forms the active species is controversial. Asano et al. proposed a cationic redox mechanism for Co_3O_4 where coordinatively unsaturated Co^{2+} atoms in tetrahedral sites form the active species [30]. It was suggested that due to potassium promotion of Co_3O_4 an increasing number of active sites is formed. Additionally, deactivation by oxygen was reduced via facilitated desorption of oxygen resulting in an overall enhanced activity of these materials in N_2O decomposition [30]. By exchanging Fe atoms into the Co_3O_4 structure, Maniak et al. found a correlation of the catalytic activity with the exchange of Co-atoms in tetrahedral and octahedral sites [34]. With $x < 1$ in $Fe_xCo_{3-x}O_4$ only Co atoms in tetrahedral sites are supposed to be exchanged by Fe. Introducing higher amounts of Fe with $x > 1$ also Co atoms in octahedral sites are exchanged. A drastic decrease in the $T_{50\%}$ values was found caused by the substitution of Co^{3+} in octahedral sites. Therefore, they concluded that Co^{3+} atoms in octahedral sites are responsible for high catalytic activities [34]. Recently, Stelmachowski et al. prepared a set of Mg, Co and Al containing spinels to create selectively catalysts with either Co^{2+} atoms in tetrahedral sites or Co^{3+} atoms in octahedral sites. They proposed that the primary active sites are Co^{3+} atoms in octahedral sites [35]. This explains on the one hand the decrease in catalytic activity due to exchange of the octahedral Co^{3+} atoms in Co_3O_4 . But on the other hand, this does not explain why the exchange of Co^{2+} atoms by the proper amount of Mg^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} increases the catalytic activity compared to Co_3O_4 [21–23,27,28]. Furthermore, according to Krezhov et al. Mg^{2+} and Ni^{2+} show a preference for occupying octahedral sites, while Zn^{2+} prefers to occupy tetrahedral sites. In the case of Cu^{2+} , a statistical distribution among the tetrahedral and octahedral sites was described [36,37]. Furthermore, a comprehensive understanding of the influence of the crystalline bulk material composition on the exposed surface sites under reaction conditions appears indispensable to gain further insights concerning the nature and concentration of catalytically active sites.

Herein, we present a comprehensive investigation on the activity of $Cu_xCo_{3-x}O_4$ ($x = 0, 0.25, 0.5, 0.75, 1$) prepared by an alkaline free synthesis route in N_2O decomposition enabling a decoupled analysis of the contribution of copper content and dopant addition. Various alkaline (earth) metals were utilised as dopants and their influence on the catalytic activity of $Cu_xCo_{3-x}O_4$ for N_2O decomposition were investigated. The most active catalysts were investigated in the presence of NO, O_2 and H_2O examining the individual effect of these compounds and the stability of the optimum catalyst under real reaction conditions combining NO, O_2 and H_2O .

2. Experimental

2.1. Catalyst preparation

$Cu_xCo_{3-x}O_4$ ($x = 0, 0.25, 0.5, 0.75, 1$) catalysts were prepared by thermal decomposition at 600 °C of stoichiometric mixtures of metal nitrate precursors. The respective amounts of $Co(NO_3)_2 \cdot 6H_2O$ (Sigma–Aldrich) and $Cu(NO_3)_2 \cdot 3H_2O$ (Sigma–Aldrich) were dissolved in distilled H_2O , the water was evaporated at 80 °C and the resulting solid was pestle in a mortar. The solid mixture of nitrates was decomposed at 600 °C



Scheme 1. Reactions during N_2O decomposition. (1) Dissociative adsorption of N_2O , (2) O_2 desorption via Langmuir–Hinshelwood mechanism, (3) O_2 desorption via Eley–Rideal mechanism.

for 3 h in air. The preparation of alkaline (earth) doped catalysts (Na, K; Sr, Ba) followed the same procedure by adding the corresponding metal nitrate to the mixture and a molar ratio of $n[\text{M}]/(n[\text{Co}] + n[\text{Cu}]) = 0.005\text{--}0.05$ was used.

2.2. Catalyst characterisation

X-ray powder diffraction (XRD) and elemental analysis of the powdered catalysts were carried out prior and after the reaction. XRD patterns were recorded on a Siemens D5000 using Cu-K α radiation. Temperature programmed desorption of oxygen (TPD-O₂) and TPR was performed on a Quantachrome ChemBET Pulsar using a thermal conductivity detector. Prior to the temperature programmed analysis, the catalysts were degassed in a flow of He at 400 °C. For TPD-O₂ analysis O₂ was adsorbed in a flow of 20 ml/min at 120 °C to avoid physisorption of O₂. For desorption of O₂ the sample was purged with He and heated up from 40 °C to 600 °C (heating rate = 20 °C/min). In TPR measurements a mixture of 5% H₂ in N₂ flowed over the sample during heating up to 600 °C (heating rate = 10 °C/min). Thermo gravimetric analysis (TGA) was performed on a Netzsch STA 409C/CD. The temperature was increased starting from 25 °C to 1000 °C with a heating rate of 5 °C/min. The elemental analysis was carried out on an Analytical Instruments Modell Spectro by inductive coupled plasma optical emission spectroscopy (ICP-OES). Prior to the analysis, the solid samples were dissolved in hot, concentrated HNO₃. Quantification of potassium was carried out at Kolbe micro labs. Prior to N₂-sorption measurements, the samples were degassed in vacuum at 110 °C for 12 h using a Quantachrome Flovac degasser. The N₂-sorption isotherms were recorded on a Quantachrome Quadrasorb SI. Specific surface area was calculated using the BET multi point method in the p/p_0 range within 0.05 and 0.21 with nitrogen as adsorbate at –196 °C.

2.3. Catalytic experiments

Catalytic tests were carried out in a fixed bed flow reactor (see Supporting information). The catalysts were tableted, pulverised and sieved into 35–60 mesh and placed into the reactor. The catalysts were pre-treated for 30 min at 400 °C in nitrogen flow and cooled down to the starting temperature. Afterwards, the reaction gas composed of 1000 ppm N₂O in N₂ as balance (ideal conditions) or 1000 ppm N₂O + 200 ppm NO + 2% O₂ + 0.5% H₂O (real conditions) was introduced into the reactor with a catalyst contact time of $W/F = 0.2 \text{ g s ml}^{-1}$ (GHSV = 54,000 h⁻¹) and the temperature was raised in steps of 40 °C starting from 130 °C to 690 °C. Each temperature was set constant for 30 min. The effluent gases of the reactor were analysed by infrared spectroscopy using a Agilent Cary 660 equipped with a Pike 2 m heated gas cell. Prior to each catalytic run, the incoming N₂O concentration ($c(\text{N}_2\text{O})_{\text{in}}$) was

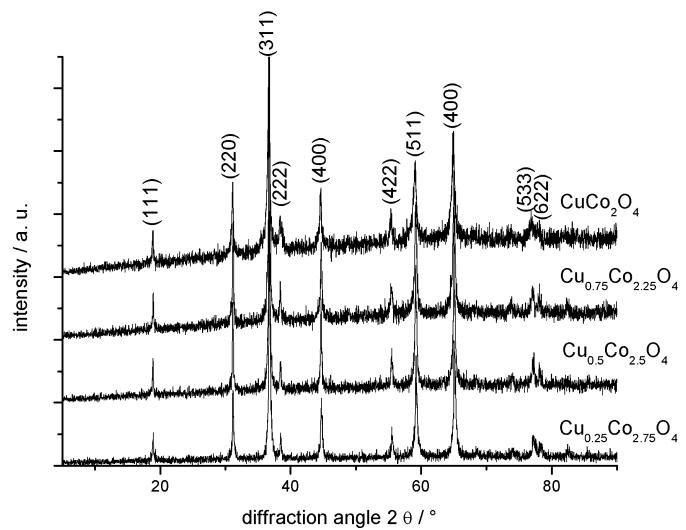


Fig. 1. X-ray diffraction patterns of $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ with indexing of the spinel phase reflexes.

determined and the N₂O conversions were estimated according to $X(\text{N}_2\text{O}) = [(c(\text{N}_2\text{O})_{\text{in}} - c(\text{N}_2\text{O})_{\text{out}})/c(\text{N}_2\text{O})_{\text{in}}] \times 100\%$.

During the stability test, a constant temperature of 400 °C and real reaction conditions were used. At all times, a catalyst contact time of $W/F = 0.2 \text{ g s ml}^{-1}$ was used.

3. Results and discussion

3.1. Catalyst characterisation

X-ray diffraction patterns of the materials without doping prior to their application in catalysis are summarised in Fig. 1. In accordance to ICDD entry 00-042-1467 all indexed reflexes correspond to the space group Fd3m, which is the typical space group of spinels. Furthermore, no reflexes of other phases such as CuO or CoO, which could result from undesired side-reactions, are present. Beside this, all compounds show very distinct reflexes and only small baseline drifts at higher copper ratios. This is caused by the use of Cu-K α -radiation during analysis. In line, no amorphous compounds formed and all prepared materials are pure spinel phase catalysts. Diffraction pattern of doped spinels (not shown) confirm as well the presence of the pure spinel phase. The lattice parameters a_0 of the different catalysts are presented in Table 1. By increasing the amount of copper in the system the lattice parameter increase indicating the incorporation of copper into the unit cell of the spinel. Doping of the catalysts with K does not influence the lattice parameter. XRD patterns detected after catalytic runs do not differ from the patterns recorded prior to catalysis providing evidence that no structural changes occur during catalysis.

Table 1

Overview of lattice parameters a_0 , specific surface areas S_{BET} , ratios between Cu and Co based on elemental analysis (ICP-OES), molar amount of O₂ desorbed from TPD-O₂ measurements and molar ratio of potassium within the compounds for $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$.

Catalyst	$a_0/\text{\AA}$	$S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	$n(\text{Cu})/n(\text{Co})_{\text{ICP-OES}}$	$n(\text{K})/[n(\text{Cu}) + n(\text{Co})]$	$n(\text{O}_2)_{\text{des}}/10^{-6} \text{ mol/g}$
Co_3O_4	8.09	4.2	0	–	13.23
$\text{Cu}_{0.25}\text{Co}_{2.75}\text{O}_4$	8.10	26.4	0.07	–	1.85
$\text{Cu}_{0.5}\text{Co}_{2.5}\text{O}_4$	8.11	14.2	0.15	–	7.26
$\text{Cu}_{0.75}\text{Co}_{2.25}\text{O}_4$	8.11	7.3	0.31	–	5.41
CuCo_2O_4	8.13	4.8	0.47	–	4.55
K-Co ₃ O ₄	8.09	6.3	0	0.007	15.61
K-Cu _{0.25} Co _{2.75} O ₄	8.09	6.5	0.08	0.008	8.04
K-Cu _{0.5} Co _{2.5} O ₄	8.11	7.7	0.15	0.009	9.12
K-Cu _{0.75} Co _{2.25} O ₄	8.12	4.7	0.30	0.007	11.13
K-CuCo ₂ O ₄	8.13	6.3	0.44	0.009	7.38

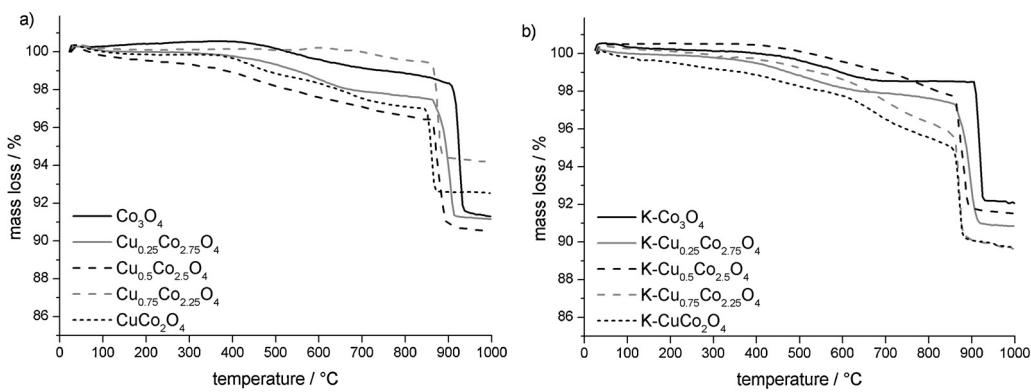


Fig. 2. Thermogravimetric analyses of (a) $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ and (b) $\text{K-Cu}_x\text{Co}_{3-x}\text{O}_4$.

All molar ratios of the metals in the spinel were confirmed by elemental analysis to fit to the desired ratios expected from the corresponding elemental formula (see Table 1). Deviations correspond to the uncertainties of the analysis. No change in composition was detected after application of the materials in catalysis. The determined S_{BET} were calculated using the BET-theory in the range of $p/p_0 = 0.05–0.21$. All spinels show very low specific surface areas in the range of $4–27 \text{ m}^2 \text{ g}^{-1}$ (see Table 1).

In the case of undoped $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ spinels, the specific surface area slightly increases for decreasing copper amounts. In contrast, no clear trend of the specific surface areas can be observed for potassium doped spinels. Sorption isotherms (not shown) correspond to a type II isotherm shape, indicating the absence of micro- or mesoporosity. Therefore, the specific surface area of the materials is mainly related to the external surface of the crystalline particles. Thermogravimetric analyses (TGA) for materials with varying Cu amounts in $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ confirm high thermal stability up to temperatures of at least 850 °C (Fig. 2). Decreasing the amount of Cu in the material leads to higher thermal stability. In the temperature region of 300–600 °C, a weight loss occurs corresponding to the thermally induced formation of oxygen vacancies; however, no correlation with the Cu amount in the samples could be observed. At temperatures above 850 °C, an endothermic phase transition takes place. The phase transformation is completed at about 920 °C with a mass loss of >10%. XRD measurements after TGA indicate a separation of the mixed spinels into Co_3O_4 , CuO and a small amount of CoO . The higher the amount of Cu in the sample the lower is the temperature for this transformation. Apparently, the presence of Cu facilitates the thermally induced phase separation.

Although, oxygen vacancies have been discussed as active sites important for an efficient decomposition of N_2O , hardly any attempts have been made to investigate the number and nature of oxygen vacancies on the surface of solids qualitatively or quanti-

tatively, respectively. We studied the influence of copper on the desorption of oxygen as measure of oxygen vacancies applying TPD- O_2 analysis. Desorption of weakly chemisorbed O_2 -species takes place at temperatures between 150 and 400 °C (Fig. 3a and b) and can be correlated to the number of oxygen vacancies produced during materials synthesis. Only at temperatures higher than 400 °C, thermal induced O_2 -vacancies form. Interestingly, TPD- O_2 analysis indicates that the presence of Cu in the sample decreases the molar amount of desorbed O_2 compared to Co_3O_4 . In line, the number of O_2 -vacancies on the surface decreases for Cu containing spinels. Furthermore, K-doped $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ materials can desorb more oxygen from the surface compared to $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ emphasising a higher number of O_2 -vacancies on the surface. However, desorption is much broader. Additionally, the number of desorbed O_2 molecules does not follow a linear trend corresponding to the Cu amount. A maximum is reached for $x=0.75$ and $x=0.5$ for doped and undoped $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$, respectively. This indicates for Cu containing materials that $\text{K-Cu}_{0.75}\text{Co}_{2.25}\text{O}_4$ has the highest concentration of O_2 vacancies on the surface in the set of doped catalysts and $\text{Cu}_{0.5}\text{Co}_{2.5}\text{O}_4$ for the undoped materials. Nevertheless, overall Co_3O_4 and $\text{K-Co}_3\text{O}_4$ possess the highest number of oxygen vacancies.

Temperature programmed reduction (TPR) emphasises a shift in reduction temperature to 100 °C lower temperatures for Cu containing spinels compared to Co_3O_4 (Fig. 4). In contrast, the Cu amount in $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ does not cause a significant change of the reduction temperature. Obviously, the presence of Cu facilitates reduction of the materials. Only a slight shoulder appears for all spinels; both the reduction from +III to +II and the following reduction from +II to 0 takes place at nearly the same temperature for Co_3O_4 as well as for the Cu exchanged spinels, respectively.

For potassium doped catalysts in TPR two distinct peaks occur. The reduction from +III to +II is clearly separated from the reduction

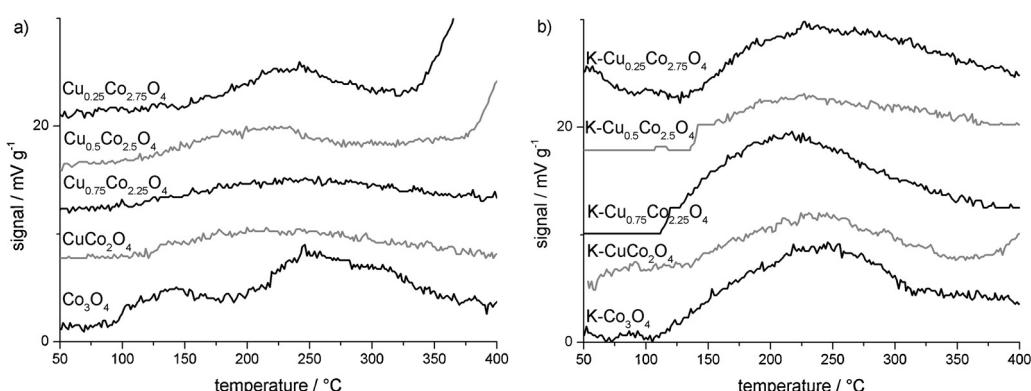


Fig. 3. TPD- O_2 profiles of (a) $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ and (b) $\text{K-Cu}_x\text{Co}_{3-x}\text{O}_4$.

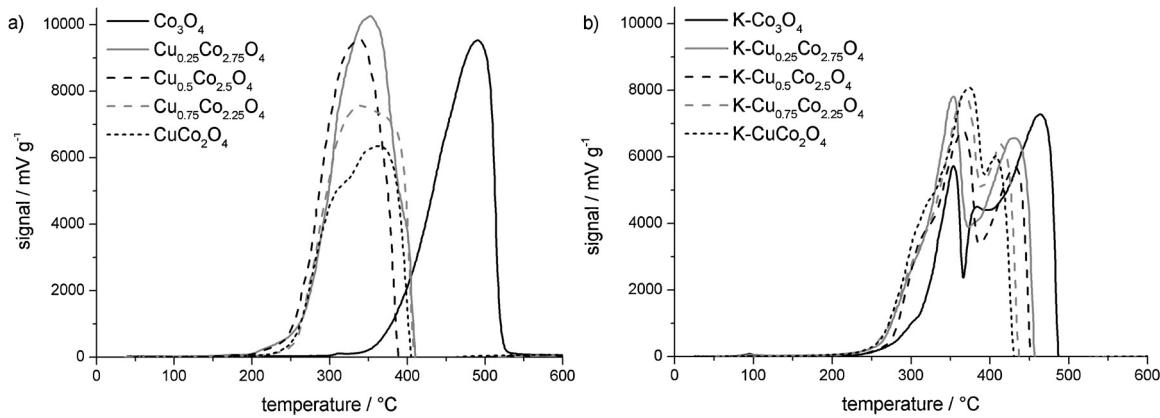


Fig. 4. TPR profiles of (a) Cu_xCo_{3-x}O₄ and (b) K-Cu_xCo_{3-x}O₄.

of +II to 0. The first reduction exhibits a slight shift to higher temperature for increasing Cu amount in the material together with a broadening of the signal. The second reduction peak exhibits a stronger dependency on the Cu amount. For all Cu amounts, this peak is shifted to at least 60 °C higher temperatures compared to the corresponding dopant-free spinel. In line, potassium promotion seems to stabilize Co²⁺ ions in the presence of Cu. Only in the case of Co₃O₄, the reduction is already completed at a 25 °C lower temperature for the doped catalyst compared to undoped Co₃O₄.

3.2. N₂O decomposition over Cu_xCo_{3-x}O₄

The catalytic activities of undoped Cu_xCo_{3-x}O₄ with varying amounts of Cu have been investigated in the decomposition of N₂O (Fig. 5). Compared to the activity of pure Co₃O₄, all catalysts containing Cu exhibit superior catalytic activity. Interestingly, low amounts of Cu promote the activity of the catalysts more significantly compared to higher amounts of Cu. With an exchange of $x=0.25$ units of Co by Cu, the reaction already starts at 250 °C, and the temperature for full N₂O decomposition is decreased to 410 °C in idealised reaction conditions. In contrast, the reaction with pure Co₃O₄ as catalyst does not start until 370 °C and full conversion requires temperatures as high as 650 °C. Surprisingly, increasing the number of Co atoms exchanged by Cu does not lead to a further increase in activity compared to Cu_{0.25}Co_{2.75}O₄. Nevertheless, still superior activity compared to Co₃O₄ is reached. Considering the discussed TPD-O₂ measurements with a maximum amount of oxygen desorbed for Co₃O₄ (Table 1, Fig. 3), the concentration of oxygen vacancies appears not to be the crucial factor for high activity at low reaction temperatures. Instead, optimum redox properties via incorporation of Cu into the spinels seem to be beneficial. This points to a synergistic behaviour between Cu and Co atoms for low amounts of Cu in the catalyst. In line with the decrease of the number of further Co atoms, the catalytic activity decreases as well. This indicates that even if Cu is integrated, the catalytic active metal should be Co. However, the influences of bulk composition on active surface sites in N₂O decomposition are not fully understood yet. But as Cu is expected to occupy both the tetrahedral and octahedral sites in the spinel [36,37], it can currently not be distinguished whether Co²⁺ or Co³⁺ forms the active species.

3.3. N₂O decomposition over potassium-doped K-Cu_xCo_{3-x}O₄

For Co₃O₄ catalysts, a doping with alkaline (earth) metals and especially potassium is known to increase the catalytic activity in N₂O decomposition. In order to produce highly active catalysts, we tested the influence of selected dopants with varying molar amounts on the activity of Cu_{0.25}Co_{2.75}O₄. As summarised in Fig. 6,

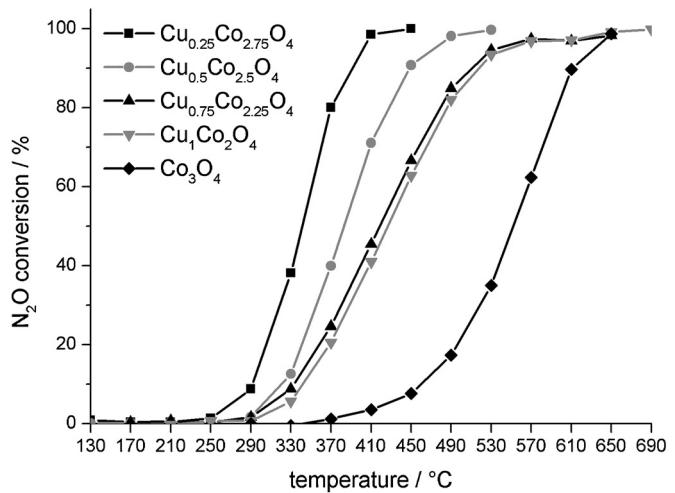


Fig. 5. N₂O conversion of Cu_xCo_{3-x}O₄ with $0 \leq x \leq 1$. Reaction conditions: c(N₂O)=1000 ppm, N₂ balance, W/F=0.2 g s mL⁻¹.

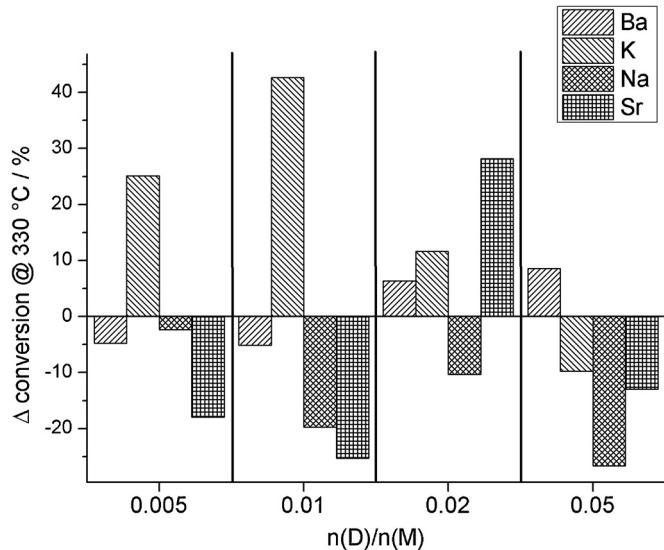


Fig. 6. Influence on catalytic activity due to variation of dopants (Ba, K, Na, Sr) and amount of doping ($n(D)/[n(Co)+n(Cu)] = 0.005–0.05$) on the catalytic activity of Cu_{0.25}Co_{2.75}O₄ tested in ideal conditions at a reaction temperature of 330 °C.

doping with barium, potassium and strontium facilitates superior activity compared to the undoped material, while sodium causes a loss in activity over the whole investigated concentration range.

Na atoms migrate into the spinel due to the small ionic radius of Na compared to the other dopants [30]. Hence, migration of Na into the bulk changes the electronic features in an impulsive way. Sr and Ba only promote the catalytic activity for molar ratios of dopant of 0.02 and 0.05, respectively. Optimum results are achieved for a molar ratio of 0.01 of potassium enabling the maximum increase in catalytic activity compared to undoped $\text{Cu}_{0.25}\text{Co}_{2.75}\text{O}_4$. Consequently, a careful adjustment of amount and type of dopant is necessary for individual materials.

For this reason, a doping with a molar ratio of 0.01 of potassium is used for further investigations. To elucidate the influence of doping for materials with different Cu content, the activity of 0.01K- $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ with varying amounts of Cu was studied (Fig. 7). For all spinel compositions, potassium doping increases the N_2O decomposition activity compared to potassium-free catalysts. Therein, catalysts with higher degree of Co exchange by Cu of $x=1$ and 0.75 show comparable activities to 0.01K- Co_3O_4 . But again the activity increases as the Cu amount is decreased to $x=0.25$. With 0.01K- $\text{Cu}_{0.25}\text{Co}_{2.75}\text{O}_4$ as catalyst the decomposition of N_2O starts at a temperature as low as 170 °C and full conversion is already achieved at 330 °C compared to 410 °C for the undoped catalyst. Overall, adjusting the type and concentration of dopant enables superior catalytic activity with up to 80 °C lower temperatures for full conversion. Comparing 0.01K- $\text{Cu}_{0.25}\text{Co}_{2.75}\text{O}_4$ to pure Co_3O_4 , the temperature for full conversion could be even decreased by 320 °C.

All K-doped catalysts exhibit higher activity together with a higher number of O₂-vacancies than their undoped equivalent. Therefore, even if O₂-vacancies are not the active species, they do have a positive influence on the overall catalytic activity. This could be due to enhanced mobility of surface atoms facilitating desorption of produced oxygen for a reaction occurring via a Langmuir–Hinshelwood mechanism (Scheme 1). Nevertheless, the catalyst with the highest number of O₂-vacancies does not possess the highest catalytic activity. Consequently, further investigations are necessary to elucidate the contribution of O₂-vacancies and the influence of changes of the electronic structure of the catalysts due to K doping on the catalytic activity of the materials.

3.4. Variation of reaction conditions

The most active catalyst 0.01K- $\text{Cu}_{0.25}\text{Co}_{2.75}\text{O}_4$ has been investigated under different reaction conditions to obtain further insights concerning the performance and stability of this material. With

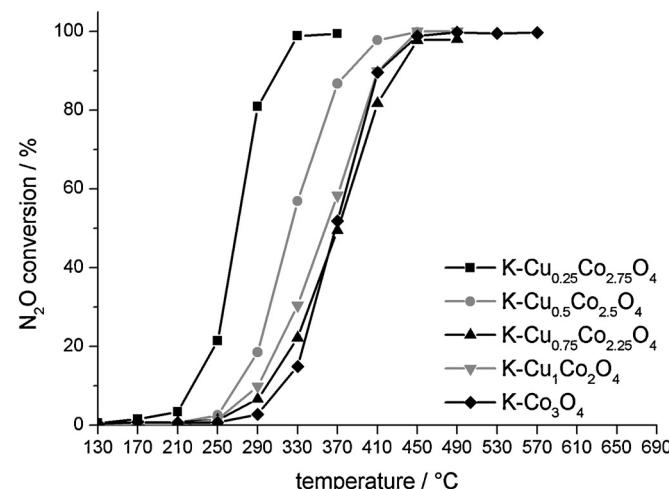


Fig. 7. Conversions of K-Cu_xCo_{3-x}O₄ catalysts ($0 \leq x \leq 1$; $n(\text{K})/[n(\text{Co}) + n(\text{Cu})] = 0.01$) in N_2O decomposition at increasing temperature. Reaction conditions: $c(\text{N}_2\text{O}) = 1000 \text{ ppm}$, N_2 balance, $W/F = 0.2 \text{ g s mL}^{-1}$.

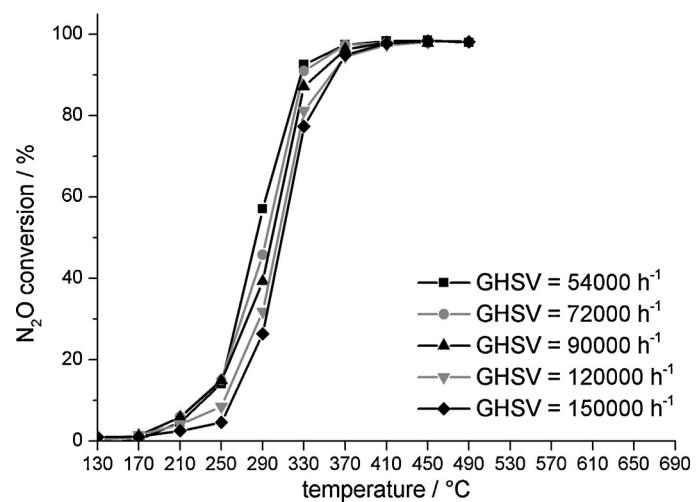


Fig. 8. Variation of GHSV for 0.01K- $\text{Cu}_{0.25}\text{Co}_{2.75}\text{O}_4$ as catalyst in idealised conditions (1000 ppm N_2O).

increasing GHSV in ideal conditions only a minor loss of activity is observed (Fig. 8). The onset of the reaction remains at a constant temperature of 170 °C.

In tail gases of nitric acid production, gases such as NO, O₂ and water vapour are always present. Therefore, these gases were added separately into the reactant mixture and also all together to investigate the catalytic performance in realistic conditions and the influence of the single gases, respectively. Fig. 9 summarises the conversions in presence of the different gases for undoped $\text{Cu}_{0.25}\text{Co}_{2.75}\text{O}_4$ as catalyst. As expected, the catalyst performs best in ideal conditions. Comparing the influence of the different gases, an addition of 2% O₂ and 0.5% H₂O, respectively, causes a more significant drop in activity than the addition of 200 ppm NO to the reactant mixture. By adding all gases together into the mixture, the individual inhibitory effects of the single gases do not sum up indicating a competition for adsorption of the different compounds on the active centres. Instead, the performance in real conditions is only slightly decreased compared to an exclusive addition of H₂O. A potential explanation relates to high affinity of water to adsorb on the active sites. Anyway, the catalyst still shows high activity for decomposing N_2O and full conversion is reached at 570 °C which is still 80 °C lower than Co_3O_4 in ideal conditions.

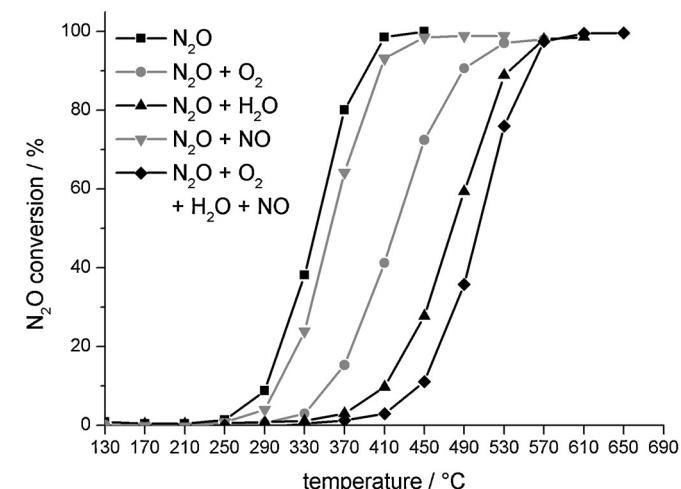


Fig. 9. Performance of $\text{Cu}_{0.25}\text{Co}_{2.75}\text{O}_4$ in N_2O decomposition during the addition of 2% O₂, 0.5% H₂O, 200 ppm NO, respectively, and in real conditions (GHSV = 54,000 h⁻¹).

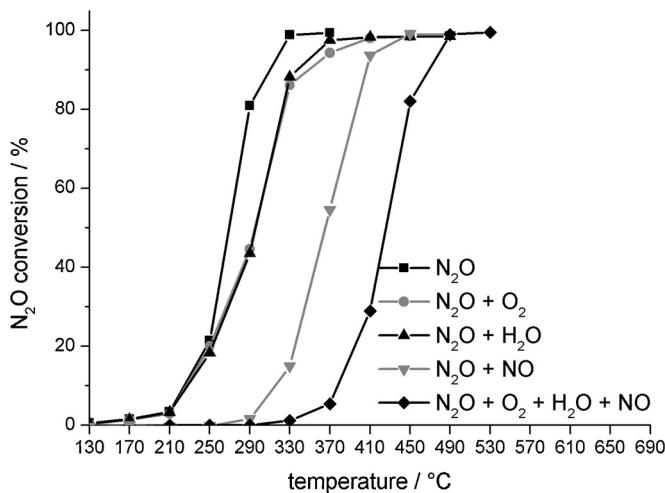


Fig. 10. Performance of 0.01K-Cu_{0.25}Co_{2.75}O₄ in N₂O decomposition during the addition of 2% O₂, 0.5% H₂O, 200 ppm NO, respectively, and in real conditions (GHSV = 54,000 h⁻¹).

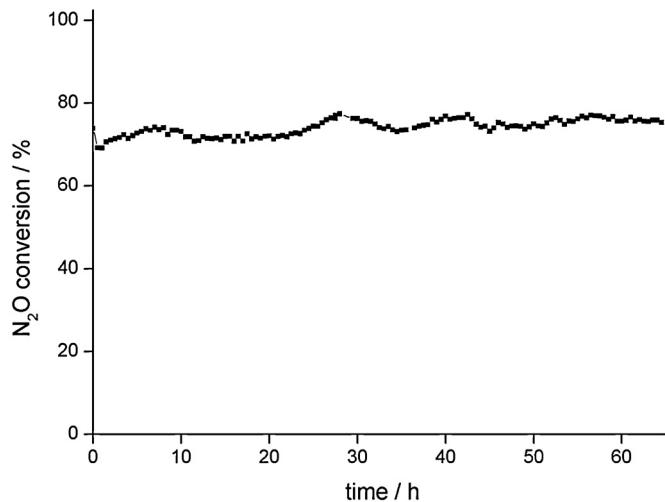


Fig. 11. Stability test at 400 °C realistic reaction conditions. GHSV = 54,000 h⁻¹.

The influence of varying gas mixtures on the catalytic activity has also been studied for 0.01K-Cu_{0.25}Co_{2.75}O₄ (Fig. 10). Surprisingly, addition of O₂ as well as H₂O to the reaction leads to only slight decrease in activity at higher reaction temperatures. Furthermore, the effect of these two gases is comparable and much less pronounced than in the case of undoped Cu_{0.25}Co_{2.75}O₄. We assign this observation to facilitated oxygen desorption due to doping with K. Interestingly, inhibition by NO is much more pronounced for the K-doped catalyst than for the undoped material. The origin of this effect is not fully understood yet but points towards altering of the reaction pathway and/or the adsorption–desorption behaviour. The inhibitory effects of the single gases appear to sum up for a gas mixture with all compounds. However, the potassium doped catalyst shows still high activities at relatively low reaction temperatures. The reaction starts in real conditions at a temperature as low as 330 °C and full conversion is achieved at 490 °C.

As high stability under reaction conditions is necessary for a technical application, the performance of 0.01K-Cu_{0.25}Co_{2.75}O₄ under real reaction conditions at a constant temperature of 400 °C was investigated (Fig. 11). Over a timescale of 65 h, high and stable conversion of 70–75% with minor fluctuations was observed. Though, these investigation is certainly no sufficient to verify stability for an application of the material on industrial scale, the

experiments confirm a high chemical stability during continuous flow conditions and no continuous deactivation in the presence of NO, O₂ and H₂O.

Currently, Fe-ZSM-5 is applied industrially reaching 80% conversion at 450 °C in a stability test under comparable reaction conditions [3]. 0.01K-Cu_{0.25}Co_{2.75}O₄ allows similar catalytic activity compared to Fe-ZSM-5 under realistic reaction conditions as well as compared to doubly promoted K/Zn-Co₃O₄ with a T_{50%} values of around 275 °C. One has to keep in mind, that e.g. the study of Inger et al. uses a higher N₂O concentration but a significantly lower GHSV hampering a direct comparison [26].

With regard to a commercial application, 0.01K-Cu_{0.25}Co_{2.75}O₄ could present an interesting material candidate. The temperature of 490 °C for full conversion in the presence of inhibitory gases such as H₂O, O₂ and NO is close to the temperatures of the tail gases from the HNO₃-production. Removing NO_x prior to the deN₂O stage makes the addition of reducing agents (NH₃) in the deN₂O stage and the heating up of the tail gases no longer necessary and can further reduce the temperature for the deN₂O stage. Nevertheless, to evaluate the economic potential of a commercial utilization factors such as long-term stability, ease of preparation as well as the optimum operational range are crucial. Consequently, a true evaluation of a market potential of our system would require a sensitivity analysis of major factors governing economic of N₂O decomposition on an industrial scale.

4. Conclusions

In this study, pure spinel phase Cu_xCo_{3-x}O₄ mixed oxides were synthesised by thermal decomposition of metal nitrate precursors. The catalysts were investigated in N₂O decompositions under ideal conditions confirming that the activity is strongly dependent on the amount of Cu in the unit cell. Decreasing the amount of Cu in Cu_xCo_{3-x}O₄ to x = 0.25 leads to the most active catalyst. A series of selected dopants shows that a small amount of K has the most promoting effect on the catalytic activity with superior activity for 0.01K-Cu_{0.25}Co_{2.75}O₄. TPR measurements indicate that the presence of Cu facilitates the reduction of Co³⁺ and Co²⁺, whereby K stabilises Co²⁺. The fine tuning of these changes in redox behaviour leads to highly active catalysts. For the most active catalysts of each series, the effect of additional gases present in tail gases from HNO₃ production was unravelled. A promotion by potassium seems to facilitate desorption of O₂ and H₂O from the catalyst. At the same time, the influence of NO becomes more significant compared to the undoped catalyst. Nevertheless, the optimised 0.01K-Cu_{0.25}Co_{2.75}O₄ catalyst reaches full conversion at temperatures as low as 330 °C and 490 °C under ideal and real reaction conditions respectively. Furthermore, stability tests under constant reaction conditions emphasise high stability of 0.01K-Cu_{0.25}Co_{2.75}O₄ even in the presence of NO, O₂ and water. Future studies will certainly aim for a deeper understanding of the contribution of oxygen vacancies and redox properties to catalytic activity and factors governing deactivation in the presence of NO, O₂ and water.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2015.04.002>.

References

- [1] J. Kramlich, W.P. Linak, Prog. Energ. Combust. 20 (1994) 149.
- [2] United Nations Framework Convention on Climate Change UNFCCC, Conference of the Parties 8 (2003) 28.3. (fccc/cp/2002/8 p.15).
- [3] J. Pérez-Ramírez, F. Kapteijn, K. Schöffel, J.A. Moulijn, Appl. Catal. B 44 (2003) 117.
- [4] F. Kapteijn, J. Rodriguez-Mirasol, J.A. Moulijn, Appl. Catal. B 9 (1996) 25.
- [5] G. Centi, A. Galli, B. Montanari, S. Perathoner, A. Vaccari, Catal. Today 35 (1997) 113.
- [6] K. Yuzaki, T. Yarimizu, K. Aoyagi, S. Ito, K. Kunimori, Catal. Today 45 (1998) 129.
- [7] J. Haber, T. Machej, J. Janas, M. Nattich, Catal. Today 90 (2004) 15.
- [8] M. Hussain, A. Parveen, D. Fino, N. Russo, J. Environ. Chem. Eng. 1 (2013) 164.
- [9] M. Konsolakis, I.V. Yentekakis, G. Pekridis, N. Kaklidis, A.C. Psarras, G.E. Marnellos, Appl. Catal. B 138–139 (2013) 191.
- [10] A. Satsuma, H. Maeshima, K. Watanabe, K. Suzuki, T. Hattori, Catal. Today 63 (2000) 347.
- [11] R. Drago, K. Jurczyk, N. Kob, Appl. Catal. B 13 (1997) 69.
- [12] S. Kannan, C.S. Swamy, Catal. Today 53 (1999) 725.
- [13] J.N. Armor, T.A. Braymer, T.S. Farris, Y. Li, F.P. Petrocelli, E.L. Weist, S. Kannan, C.S. Swamy, Appl. Catal. B 7 (1996) 397.
- [14] U. Chellam, Z.P. Xu, H.C. Zeng, Chem. Mater. 12 (2000) 650.
- [15] M. Zabilskiy, P. Djinovic, B. Erjavec, G. Drazic, A. Pintar, Appl. Catal. B. 163 (2015) 113.
- [16] Y. Wu, C. Cordier, E. Berrier, N. Nuns, C. Dujardin, P. Granger, Appl. Catal. B 140–141 (2013) 151.
- [17] J. Pieterse, S. Booneveld, R. Brink, Appl. Catal. B 51 (2004) 215.
- [18] J. Perez-Ramirez, F. Kapteijn, G. Mul, J.A. Moulijn, Catal. Commun. 3 (2002) 19.
- [19] R.S. da Cruz, A.J.S. Mascarenhas, H.M.C. Andrade, Appl. Catal. B 18 (1998) 223.
- [20] M. Schwefer, M. Groves, R. Siefert, R. Rainer, Patent EP 2286897 B1, (2003).
- [21] N. Russo, D. Fino, G. Saracco, V. Specchia, Catal. Today 119 (2007) 228.
- [22] L. Yan, T. Ren, X. Wang, D. Ji, J. Suo, Appl. Catal. B 45 (2003) 85.
- [23] L. Yan, T. Ren, X. Wang, D. Ji, J. Suo, Catal. Commun. 4 (2003) 505.
- [24] P. Stelmachowski, F. Zasada, G. Maniak, P. Granger, M. Inger, M. Wilk, A. Kotarba, Z. Sojka, Catal. Lett. 130 (2009) 637.
- [25] M. Inger, P. Kowaliuk, M. Saramok, M. Wilk, P. Stelmachowski, G. Maniak, P. Granger, A. Kotarba, Z. Sojka, Catal. Today 176 (2011) 365.
- [26] M. Inger, M. Wilk, M. Saramok, G. Grzybek, A. Grodzka, P. Stelmachowski, W. Makowski, A. Kotarba, Z. Sojka, Ind. Chem. Res. 53 (2014) 10335.
- [27] V. Srinivasan, R. Sundararajan, Appl. Catal. 73 (1991) 165.
- [28] B.M. Abu-Zied, S.A. Soliman, S.E. Abdellah, J. Ind. Eng. Chem. 21 (2015) 814.
- [29] C. Ohnishi, K. Asano, S. Iwamoto, K. Chikama, M. Inoue, Catal. Today 120 (2007) 145.
- [30] K. Asano, C. Ohnishi, S. Iwamoto, Y. Shioya, M. Inoue, Appl. Catal. B 78 (2008) 242.
- [31] Z. Dou, H.J. Zhang, Y.F. Pan, X.F. Xu, J. Fuel Chem. Tech. 42 (2014) 238.
- [32] M. Haneda, Y. Kintaichi, N. Bion, H. Hamada, Appl. Catal. B 46 (2003) 473.
- [33] F. Zasada, P. Stelmachowski, G. Maniak, J.-F. Paul, A. Kotarba, Z. Sojka, Catal. Lett. 127 (2009) 126.
- [34] G. Maniak, P. Stelmachowski, J.J. Stanek, A. Kotarba, Z. Sojka, Catal. Commun. 15 (2011) 127.
- [35] P. Stelmachowski, G. Maniak, J. Kaczmarczyk, F. Zasada, W. Piskorz, A. Kotarba, Z. Sojka, Appl. Catal. B 146 (2014) 105.
- [36] K. Krezhev, P. Konstantinov, Acta Phys. Hung. 75 (1994) 243.
- [37] K. Krezhev, P. Konstantinov, Physica B 234–236 (1997) 157.